

<https://doi.org/10.3176/oil.1997.4.05>

SOME COMMON TRAITS OF THERMAL DESTRUCTION OF OIL SHALES FROM VARIOUS DEPOSITS OF THE WORLD

V. YEFIMOV

S. DOILOV

I. PULEMYOTOV

Oil Shale Research Institute
Kohtla Järve, Estonia

The physical and chemical properties of low- and high-sulfur oil shales from 36 deposits throughout the world, and of their retorting products have been investigated and generalized. Basing on the oil qualities, the shales may be divided into three main groups: yielding paraffinic, high-sulfur, and oxygen-compound-rich oils.

On the basis of the distribution of sulfur between retorting products, the oil shales from various deposits of the world tested in the standard Fischer assay may be divided into four groups. The first group comprises the oil shales whose retorting yields semicoke containing 100-70 % of the total sulfur (low-sulfur shales). The respective amount of sulfur in semicoke of other shales is 70-50 % (II, transitional group), 50-30 % (III), and 30-20 % (IV), the last two groups comprise high-sulfur shales. Other changes in physical and chemical properties of retorting products may be traced back to be in a good correlation with this feature.

Oil shales of the world may be divided into rich and pure ones on the basis of the oil yield of retorting in the standard Fischer assay. The oil yield 15 % marks the distinction between poor and rich oil shales. Besides, oil shales may be divided into low- (<2 %) and high- (>2 %) sulfur shales.

The results of our research on high- and low-sulfur oil shales from various deposits of the world using standard methods [1,2] offer a good opportunity to examine some common traits of physical and chemical properties of initial shales and their products. These results may also be applied in classifying world oil shales for technological purpose.

Table 1. A General Technological Classification Proposed for Oil Shales from Various Deposits of the World

Deposit	Sample number	Distribution of sulfur between retorting products, %			Sulfur content of initial shale, %			Sulfur content, %		Share of organic S in total, %	H ₂ S content of gas, g/m ³	Oil density, kg/m ³
		Semicoke	Oil	Gas	Total	Pyrite	Organic	Oil	Semicoke			
1	2	3	4	5	6	7	8	9	10	11	12	13
First group												
Anin, Banata	1	98.5	3.6	traces	0.67	0.51	0.16	0.50	0.75	23.9	traces	913
Eckibastuse	2	89.1	1.7	traces	1.32	1.08	0.23	0.44	1.30	17.4	traces	915
Maoming	3	87.6	2.6	2.8	1.22	0.98	0.08	0.31	1.28	6.6	10	909
Ust-Kamenogorsk	4	87.5	8.7	3.5	1.00	—	—	0.80	1.00	—	12	906
Stuart	5	85.6	4.1	2.6	1.00	—	—	0.60	1.00	—	10	897
Fushun	6	85.3	2.3	3.6	0.78	0.55	0.12	0.48	0.74	15.4	10	893
Gurkovo-Nikolayev	7	84.2	3.4	3.2	0.38	0.31	0.07	0.46	0.40	18.4	6	878
Kenderlyck	8	80.5	9.4	6.2	2.10	—	0.64	1.00	2.35	30.5	41	923
Paraiba valley: papery lump-sized	9 10	72.8 72.6	17.8 5.7	2.9 14.6	1.28 1.60	0.55 0.54	0.57 0.89	1.10 2.30	1.30 1.30	44.5 55.6	13 123	910 920
Aleksinac	11	70.0	5.1	14.8	2.78	2.50	0.23	1.75	2.29	8.3	133	908
Change limits of main characteristics, %												
		100-70	2-10	traces-15								
Second group												
Huadian	12	68.4	5.7	21.4	1.20	—	—	0.43	1.1	—	62	899
Boltysh	13	67.7	10.2	20.8	1.40	1.11	0.17	0.82	1.3	12.1	61	898
Ukhta	14	64.5	7.1	28.0	0.39	—	—	0.60	0.3	—	71	975
Luban	15	59.5	11.0	17.0	1.6	1.1	0.40	2.0	1.1	25.0	131	925
Mae Sot	16	59.2	12.6	28.6	0.87	0.56	0.28	0.6	0.69	32.2	78	889
Breznik	17	57.5	5.3	41.5	2.47	2.27	0.12	1.35	1.7	4.9	363	934
Estonian	18	55.4	9.6	39.0	1.9	1.3	0.55	0.84	1.5	28.9	206	968

Table 1. A General Technological Classification Proposed for Oil Shales from Various Deposits of the World (end)

1	2	3	4	5	6	7	8	9	10	11	12	13	
Green River	19	53.3	12.5	20.6	0.65	0.35	0.28	0.84	0.4	43.1	75	927	
Verkhnesinevid	20	65.4	7.1	10.8	2.68	2.0	0.58	5.6	1.9	21.6	168	983	
Irati	21	65.2	2.2	24.4	4.2	4.01	0.15	1.3	3.1	0.4	405	918	
Baisun	22	55.7	11.8	—	4.15	3.28	0.82	4.2	2.94	19.8	—	962	
Sangruntau	23	53.3	10.4	25.2	4.57	2.26	1.52	7.8	2.87	33.3	302	973	
Urtbulak	24	52.4	12.4	34.2	4.56	—	—	6.0	3.24	—	273	972	
Change limits of main characteristics, %													
		70-50	5-15	10-40								0-35	
Third group													
Timahdit, test 13*	25	43.9	20.1	35.1	3.07	1.38	1.49	7.1	1.6	48.5	346	975	
Sysol	26	42.0	13.5	35.3	3.4	1.43	1.85	4.8	1.78	54.4	281	973	
Kashpir	27	41.8	17.4	40.9	3.7	1.7	1.8	7.4	1.91	48.6	391	1027	
Timahdit, test 11*	28	40.9	22.2	44.7	1.77	0.73	0.95	7.14	0.8	53.7	349	961	
Kotsebinsk	29	38.7	21.3	45.8	6.06	1.51	4.22	8.5	3.25	69.6	454	1013	
Chagan	30	38.5	22.3	44.5	4.14	1.13	2.78	7.12	2.1	67.2	349	1009	
Timahdit, test 12*	31	37.0	21.3	38.1	2.37	0.81	1.46	7.02	1.0	61.6	296	974	
El-Lajun	32	30.35	25.0	44.65**	3.43	1.09	2.24	6.6	1.26	65.3	130	—	
Change limits of main characteristics, %													
		50-30	15-25	35-50									
Fourth group													
Rubezhansk	33	28.7	30.0	53.3	4.69	0.67	3.94	6.69	2.15	84.0	353	1010	
Senoman	34	28.7	33.9	52.7	2.03	0.30	1.63	10.16	0.66	80.3	317	1010	
Perelyub, seam I	35	24.5	24.3	52.7	6.08	1.11	4.85	7.39	2.24	80.0	517	1009	
seam II	36	20.9	27.0	50.7	5.80	0.59	5.13	7.5	1.9	88.4	420	943	
Change limits of main characteristics, %													
		30-20	25-35	40-55								80-90	

* Shale sample number as given in [1].

** The amount of sulfur converted into gas is determined by difference 100 - 30.35 - 25.0 = 44.65, just as retort gas contains besides H₂S notable amounts of other kinds of sulfur (probably as thiophenes).

Oil shale samples studied by us may be divided into three main groups according to characteristics of their retort oils [3].

- Oil shales yielding low-sulfur paraffinic oils
- Oil shales yielding high-sulfur oils
- Oil shales yielding oils with a very high content of oxygen compounds (the most typical representative of this group is the oil shale - kukersite - of the Baltic shale basin)

However, technological classification of oil shales from different deposits requires establishing universally applicable parameters characterizing the physical and chemical properties of oil shales. In search of suitable parameters reflecting general features of thermal destruction of oil shales from any deposit, we have focused on distribution of sulfur in the products of retorting, first of all, on the amount of sulfur transferred into semicoke. All oil shale samples studied by us may be placed under one common regularity on the basis of this property. As seen from Table 1, the share of sulfur transferred into semicoke decreases with the increase in the amount of sulfur present in the initial shale, accompanied by the increase in the sulfur content of oil and gas.

The comparison of all studied oil shale samples on the basis of sulfur distribution upon retorting enables to differentiate between four distinct groups (Tables 1 and 2), and such a distribution of sulfur applies to all high- and low-sulfur shales of the world. The first group includes only low-sulfur shales. The second group is a transitional one and comprises both low- and high-sulfur shales. The third and the fourth groups comprise only high-sulfur shales.

Table 2. Main Qualitative Characteristics of Oil Shales from Various Deposits of the World Used for Their Technological Classification

Distribution of sulfur in retorting products, %			Share of organic S in total, %	Sulfur content, %	
Semicoke	Oil	Gas		Oil shale	Oil
First group					
100-70	up to 10	up to 15	—	0.4-2.8	0.4-2.3
Second group					
70-50	5-15	10-40	0-35	0.4-6.1	0.4-10.2
Third group					
50-30	15-25	35-50	45-70	1.8-6.1	4.0-10.2
Fourth group					
30-20	25-35	35-55	80-90	1.8-6.1	4.0-10.2

Interestingly enough, high-sulfur shales are characterized by one more trait - the sulfur content of semicoke depends not only on the content of sulfur in the oil shale but even more on the share of organic sulfur in total sulfur. The regularity does not apply to low-sulfur shales yielding paraffinic oil upon retorting.

As seen from Table 1, during retorting of low-sulfur shales mostly paraffinic oils are formed. The oils obtained are characterized by decreased density values (about 900 kg/m^3), and high solidification point values - $20\text{-}30 \text{ }^\circ\text{C}$. Light-middle fractions of high-sulfur oils have quite similar chemical group composition. They are characterized by elevated content of aromatic hydrocarbons and low share of olefins. Most of the investigated oils contain only few phenols, except for the retort oils from shales of the following deposits: Estonian, Verkhnesinevid, and, to some extent, also Luban.

The highest yield of oil (on organic matter basis) are obtained from shales of the deposits Green River, Estonian, and Mae Sot. Rather high oil yields characterize oil shales from Kenderlyck, Luban, El-Lajjun, Huadian, and Breznik.

Mineral parts of Estonian, Moroccan, Syrian and Jordanian oil shales contain much calcium carbonates. Australian, Chinese, and Bulgarian oil shale mineral parts are rich in silicon compounds.

One more fact must be mentioned here. As generally known, one maximum of shale formation occurred in Cainozoic.

During Cainozoic, unique formation of lake shales formed in Green River (USA), basins in Thailand and Australia (Stuart, Randle, Condor, and others), Huadian, Fushun, and Maoming in China [4]. As seen from Table 1, oil shale samples Nos. 13, 16, 5, 12, 6, and 3 are low-sulfur ones, and the oils formed upon their retorting are paraffinic and contain small amounts of sulfur - $0.3\text{-}0.8 \%$. Oil shales from Asia contain little sulfur, and during their retorting low-sulfur oils are formed.

Acknowledgments

The authors wish to thank the Estonian Science Foundation for the support under Grant N^o 2029.

REFERENCES

1. Yefimov, V., Doilov, S., Pulemyotov., I. Research and experimental processing of high-sulfur oil shales // Oil Shale. 1995. Vol. 12, N. 4. P. 317-340.
2. Yefimov, V., Doilov, S., Pulemyotov., I. Research and experimental processing of low-sulfur oil shales // Oil Shale. 1996. Vol. 13, N. 4. P. 265-285.

3. *Yefimov, V., Doilov, S., Lööper, R., Kundel, H.* Oil shales as technological feedstock for liquid fuels production // 27th International Geological Congress, Aug. 4-14, Moscow. 1984. Vol. 7. P. 160-161.
4. *Golitsyn, M. V., Prokofyeva, L. M., Kolesnik, V. Ya., Tyurenkova, G. I.* World resources of oil shales, their mining and utilization // Energetical Resources of the World. 27th International Geological Congress, Aug. 4-14, Moscow. 1984. Vol. 1. P. 21-39.

Received October 14, 1996